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Influence of initial assumptions on the kinetic models of CO_2 gasification of chars and cokes in solid phase

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Abstract Kinetic studies of CO_2 gasification of different materials were carried out using the Geneva method in an apparatus for determining the reactivity of cokes. The main purpose of these studies was parallel analysis of the Boudouard–Bell (B–B) reaction progress on the basis of both solid-phase and gaseous products combined with the mass balance of the process. The kinetic equations involve the conversion degree of the solid (x) or gaseous phase (α) with the kinetic reaction rate constant. It was proved that the mathematical form of the mass balance is similar to the simplest kinetic equation, in which the kinetic constant k is replaced by the known process constant C. Complete kinetic description of the B–B reaction is determined by adopting initial conditions and taking into account the chemical reaction that occurs in a short time interval.

Keywords Solid fuels · Gasification · Boudouard–Bell reaction/process · The Geneva method · Mass balance · Solid-state kinetics · Gaseous-state kinetics · Initial conditions

List of symbols

a,b	Mole fraction of inert gas and coke oven gas, respectively, in Eq. (4)
α	Conversion degree of CO_2, $0 \leq \alpha \leq 1$
B	Parameter in Eqs. (33)–(36)
C_f	Free carbon sites
C(O)	Carbon sites occupied by oxygen (oxy-carbon)
C	Process constant (time^{-1})
$[CO_2]$, $[CO]$	Mole fraction, respectively, CO_2 and CO, $0 \leq [CO_2] \leq 1,\ 0 \leq [CO] \leq 1$
$f(\alpha)$, $g(\alpha)$	Function depending on the reaction mechanism
$\dot{G}$	Constant molar flow rate of carbon dioxide (mol s^{-1})
ΔH	Enthalpy of reaction (J mol^{-1})
k	Reaction rate constant (time^{-1})
k_1	Reaction rate constant of gasification reaction (Boudouard reaction) (time^{-1})
k_{-1}	Reaction rate constant of disproportionation reaction (Bell reaction) (time^{-1})
k_3	Reaction rate constant of desorption process (time^{-1})
L	Height of the coke bed Eq. (4) (cm)
λ	Extent of reaction
m	Mass (mg)
m	Parameter in Eqs. (33)–(36)
n	Number of moles or reaction order
$\dot{n}$	Molar flow rate (moles s^{-1})
p	Parameter in Eqs. (33)–(36)
Q_i^a	Net calorific value (MJ/kg)
r^2	Linear determination coefficient, $0 \leq r^2 \leq 1$
R^2	Determination coefficient in nonlinear regression, $0 \leq R^2 \leq 1$
ρ^2	Determination coefficient in equation without intercept, $0 \leq \rho^2 \leq 1$
t	Temperature (°C)
T	Absolute temperature (K)
Ψ	Structural parameter in random pore model

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$\dot{V}$	Volume flow rate of carbon dioxide ($cm^3\ s^{-1}$)
VM^{daf}	Volatile matter in dry and ash free state (%)
τ	Time (s)
x	Conversion degree of solid phase, $0 \leq x \leq 1$
z	Auxiliary coordinate in Eq. (4)

Subscripts

i Initial

Introduction

Interest in the equilibrium reaction of CO_2 reduction to carbon monoxide in the presence of carbon, called the Boudouard–Bell reaction (abbreviated B–B), was once associated with its crucial role in the steel industry. Sainte-Claire Deville had already studied this reaction in 1864 as an interesting case of dissociation. Lothian Bell (1864, 1871) investigated this reaction in blast furnace processes. Deville and Bell's works were qualitative descriptions of the examined reactions. After 1900, Octave Boudouard published a study describing the equilibrium state of coal and carbon oxides as described in detail in [1].

The Boudouard–Bell reaction is still of significant interest due to two main reasons.

1. The B–B reaction remains relevant to the blast furnace process because it is the basis for determining the main technological parameter of coke, i.e., its reactivity, which currently determined primarily by the NSC procedure (two basic indicators are determined: the coke reactivity index (CRI) and the coke strength after reaction (CSR) [2]). Previously, the Geneva method [3] was based on these considerations, and the Dahme–Junker equation [4] was used to determine coke reactivity.
2. The ability to convert solid fuels to gaseous products by the gasification of carbon carriers with carbon dioxide, which can help meet the growing demand for gaseous fuels and chemical raw materials and reduce environmental pollution [5, 6].

In the blast furnace process, the coke's reactivity to CO_2 at high temperature is expected to be minimal (1st case), while for the gasification process, high reactivity at the lowest possible temperature is required (2nd case).

The heterogeneous, endothermic chemical reaction of the carbon with CO_2, i.e., the B–B reaction, is usually written in the general form:

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H^{\circ}_{298} = +172.42\ kJ\,mol^{-1}. \tag{1}$$

The reaction (1) can be analyzed by taking into account its various aspects:

1. the course of the reaction concerning its mechanism,
2. thermodynamics,
3. the mass balance of the reaction,
4. experimental kinetics and
5. the method of implementing the reaction/process.

According to the work [7], thermodynamic considerations can be omitted from the above-mentioned approaches to the analysis of the reaction/process (1), primarily because this reaction's ideal reversibility is observed only in the gas phase in very high temperature (>2700 K) [8], as shown in Fig. 1. Another reason is the wide variety of possible raw materials to be used in reaction (1), from carbon (in practice as hexagonal graphite) to coals, chars, cokes and biomass.

Usually, the B–B reaction (1) is explained by the well-known Ergun mechanism [9]:

$$CO_2 + C_f \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} CO + C(O) \tag{2}$$

$$C(O) \xrightarrow{k_3} CO + C_f. \tag{3}$$

Assuming that the time rate of the chemical composition of the gaseous phase characterizes the kinetics of the B–B reaction (1), it should be taken into account that the reaction can occur in two stages according to reactions (2) and (3). In this case, the problem is to explain the role of the transitional form, i.e., the active complex C(O), which is not observed in the gaseous phase. As a result, one has to clarify whether the two-step B–B reaction can be confirmed by quantitative changes in the solid phase and/or by qualitative and quantitative changes in the gas phase.

This article is the continuation of discussion on the coke reactivity presented in our previous paper [10].

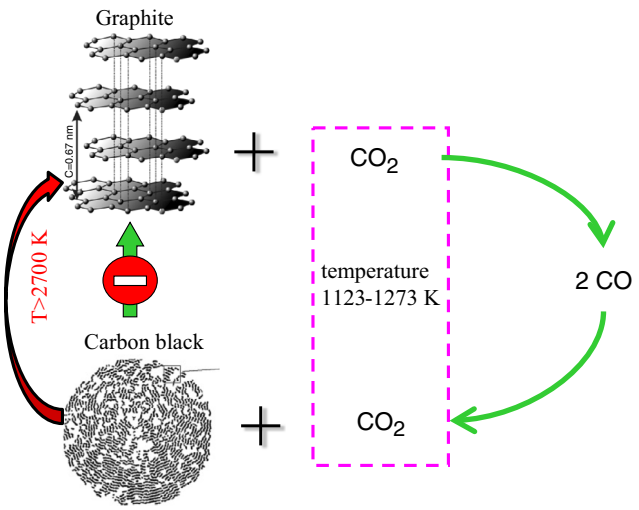

Fig. 1 Reversibility of B–B reaction for hexagonal graphite

Aim of the work

Taking into account the contradictory expectations regarding reactivity of raw materials (solid fuel) with CO_2 in various technologies, an assessment of the measurement system and methodology was performed to determine the reactivity of cokes according to the Geneva method and considering the theoretical assumptions presented by Dahme and Junker in 1955 [4]. At the initial stage of our studies, it was assumed that measuring the composition of the gas as it leaves the system without simultaneously measuring the mass loss of the solid phase is not sufficient for complete kinetic analysis of reaction (1), assuming the occurrence of the mechanism (2)–(3). Thus, in this stage of the study Dahme and Junker's kinetic model was analyzed [4].

Experimental

Methods

The measuring apparatus is shown schematically in Fig. 2. The measurement methodology was modified in contrast to the methodology used in [4] and suggested in [3]. The modified parameters for the experiments carried out according to the Geneva method [3] were the sample mass (1–7 g), particle size (1–3.15 mm), measuring time and gas flow (150 $cm^3\ min^{-1}$, i.e., 8 L h^{-1}). The experiments were carried out using the "start–stop" method. Samples of known initial "start" mass inside reaction retort were introduced into the preheated furnace, and inert gas (N_2) flowed into the retort until the sample achieve a predetermined temperature. After the sample reached that temperature, the gas flowing through the reaction retort was changed to CO_2, and the composition of gas leaving the system was tested at regular intervals (5–120 min). The contents of CO_2 and CO were determined by gas chromatography (GC) in a column packed with ShinCarbon. After the predetermined time of the experiment, the reaction retort was removed from the furnace and cooled to ambient temperature under nitrogen flow, and then, the final "stop" mass was determined.

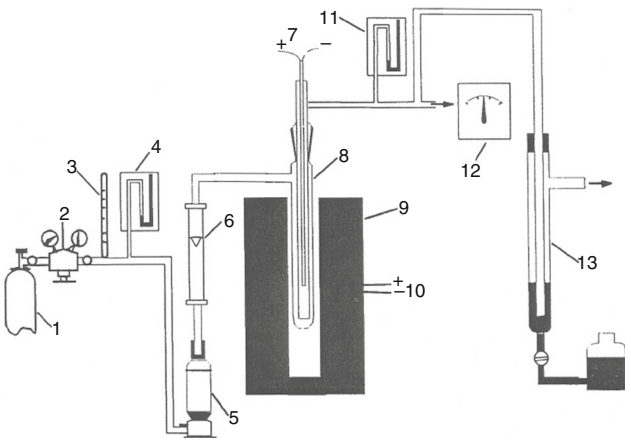

Fig. 2 Apparatus for measuring the B-B reaction kinetics according to the Geneva method: 1–CO_2 tank, 2–pressure valve, 3–thermometer, 4–pressure gauge, 5–gas dryer, 6–flowmeter, 7–thermocouple for measuring the temperature inside the sample, 8–quartz reaction retort with cover, 9–furnace, 10–thermocouple for measurement of furnace temperature, 11–pressure gauge, 12–analysis of the gaseous product composition, 13–manostat

Samples

In the equipment testing stage of the study, the following samples were used: blast furnace coke (BFC), charcoal (SBCC) and brown coal char (LCC).

For other experiments, the following archived samples were used: domestic coke (DC), semi-coke (SC) and smokeless fuel (SLF). The samples were derived from archival resources.

Basic properties of the samples tested are shown in Table 1. All samples used in the experiments were dried to a constant mass at 105 °C.

The kinetic equation of the Geneva method

The fundamental differential kinetic equation according to [4] with respect to the conversion degree of CO_2 (α) can be expressed as:

$$\frac{d\alpha}{dz} = A\frac{(1-\alpha)(1+a)}{1+\alpha+a+\frac{b}{L}z} \quad \text{where} \quad A = k\frac{T_i \cdot m_i}{T \cdot L \cdot \dot{V}} \tag{4}$$

where L is the height of the coke bed and z is an auxiliary coordinate in the range $0 \le z \le L$. This equation assumes the following equality of molar fractions is true:

$$[CO] + [CO_2] \equiv 1 \tag{5}$$

when the outlet flow from the measuring system has no other gases, i.e., inert gas (a) and coke oven gas (b). For real samples, this equality will be valid only for dry cokes

Table 1 Results of the proximate analysis of samples used in the studies in % m/m (net calorific value Q_i^a in MJ kg^{-1})

Sample	W^a	VM^a	A^a	Q_i^a
BFC—blast furnace coke	0.35	0.52	10.36	33.1
SBCC—sub-bituminous coal char	4.57	1.36	15.91	28.7
LCC—lignite coal char	7.84	3.69	10.29	22.6
DC—domestic coke "Jadwiga"	0.28	1.45	10.00	29.7
SC—semi-coke "Centrum"	6.90	8.90	17.40	27.5
SLF—smokeless fuel "Ecocoal"	1.50	10.20	11.20	28.7

with low content of volatile matter (usually $VM^{daf} < 2.5$ % is allowed).

For completely degassed and dried coke, using relation (5), the conversion degree of CO_2 in Eq. (4) becomes:

$$\alpha = \frac{1 - [CO_2]}{1 + [CO_2]} = \frac{[CO]}{2 - [CO]} \tag{6}$$

and the one-dimensional gradient of (α) with respect to the height of the sample bed (z) equals:

$$\frac{d\alpha}{dz} = A\frac{1 - \alpha}{1 + \alpha}. \tag{7}$$

By integrating over the limits $\langle 0; \alpha \rangle$ and $0 \le z \le L$, the following function is obtained [1]:

$$g(\alpha) = k\frac{T_i \cdot m_i}{T \cdot \dot{V}} \tag{8}$$

where:

$$g(\alpha) = -\alpha - 2\ln(1 - \alpha) \tag{9}$$

which, for small values of the conversion degree, leads directly to the relationship:

$$\alpha = k\frac{T_i \cdot m_i}{T \cdot \dot{V}}. \tag{10}$$

Hence, the ratio $\left(m_i/\dot{V}\right)$ performs the function of a substitute time expressed in [g s cm^{-3}].

At isothermal conditions ($T_i/T = \text{const}$) and at a constant flow of pure CO_2 ($\dot{V} = \text{const}$) for "ideal" cokes, the relationship $g(\alpha)$ or α vs m_i should be a straight line independent of time.

The results for coke (BFC), chars from sub-bituminous coal (SBCC) and brown coal (LCC) are shown in Fig. 3

Figure 3 shows the observed final conversion degree of the solid phase:

$$x = \frac{m_i - m}{m_i}, \quad 0 \le x \le 1 \tag{11}$$

where m and m_i are the actual and initial masses of the sample, assuming that the substrate is pure carbon. For other substrates sources of carbon (i.e., raw materials), the denominator in the formula (11) should be modified taking into account the mass of mineral substances [11, 12].

The experiments presented graphically in Fig. 3 unambiguously indicate that only for the most degassed fuel, i.e., coke, straight lines limiting the upper and lower end (specifying scattering of experimental data) are similar. In the case of other solid fuels, i.e., the chars and coals with high VM content, Geneva method is unhelpful, and it is necessary to simultaneously analyze the gas phase and the solid phase.

Hence, comparing changes in the gaseous and solid phases must be based on the mass balance of the reaction/process (1).

Mass balance of reaction/process (1)

Figure 4 shows a diagram of the gasification reactor using the symbols that describe the reactants and products. To prepare the mass balance, it was assumed that the reactor shown in Fig. 4 is a flow reactor because one of the substrates is CO_2. Conversely, because of the second substrate, i.e., the carbon carrier, the reactor should be treated as a batch reactor.

The final conversion degree of the solid phase in (11) can be rewritten in terms of moles of carbon as:

$$x = 1 - \frac{n}{n_i}. \tag{12}$$

So the rate of change of the conversion degree can be written as:

$$\frac{dx}{d\tau} = -\frac{1}{n_i}\frac{dn}{d\tau}. \tag{13}$$

Considering the B–B reaction stoichiometry, Eq. (13) can be written in the form:

$$\frac{dx}{d\tau} = -\frac{1}{2n_i}\frac{dn_{CO}}{d\tau} \tag{14}$$

or

$$\frac{dx}{d\tau} = \frac{\dot{n}_{CO}}{2n_i} \quad \text{where} \quad \dot{n}_{CO} = \frac{dn_{CO}}{d\tau}. \tag{15}$$

For the reaction/process under consideration (Fig. 4), the molar fraction of carbon monoxide in accordance with the definition equals:

$$[CO] = \frac{\dot{n}_{CO}}{\dot{n}_{CO} + \dot{n}_{CO_2}} \tag{16}$$

thus:

$$\dot{n}_{CO} = \dot{n}_{CO_2}\frac{[CO]}{1 - [CO]} \tag{17}$$

because:

$$\dot{n}_{CO_2} = \dot{G}(1 - \alpha) \tag{18}$$

consequently:

$$\dot{n}_{CO} = 2\dot{G}\alpha. \tag{19}$$

Substituting Eq. (19) into Eq. (15), the following equation can be obtained:

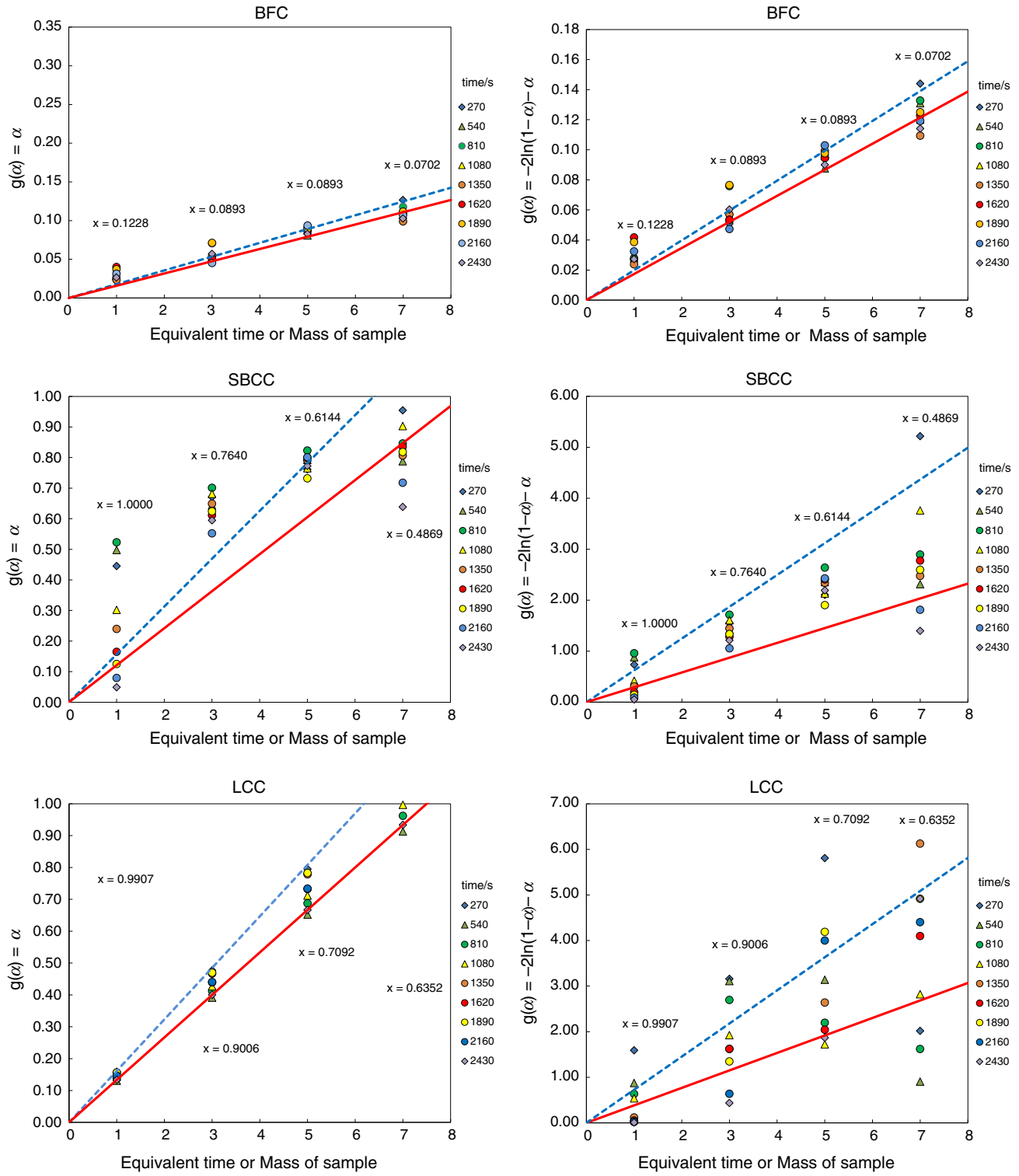

Fig. 3 Analysis of relationship (8) for two variants of the kinetic function versus substitute time represented by initial mass m_i, for fixed conditions $T, \dot{V}$ but for variable time of the process (specified in seconds)

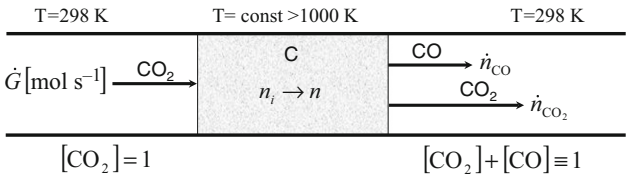

Fig. 4 Diagram of reactant flows in the Geneva reactor

$$\frac{dx}{d\tau} = \frac{\dot{G}}{n_i}\alpha. \tag{20}$$

So, for certain experimental conditions, Eq. (20) can be written as:

$$\frac{dx}{d\tau} = C \cdot \alpha \tag{21}$$

where process constant C equals:

$$C = \frac{\dot{G}}{n_i} = \frac{12 \cdot \dot{V} \cdot \rho}{44 \cdot m_i}. \tag{22}$$

Equation (22) makes it possible to combine measurements of the solid and the gaseous phase. The rate of the reaction/process (1) with respect to (real) time is directly proportional to the degree of conversion of the gaseous phase (α).

By integrating Eq. (21), one can balance the number of moles of reacted carbon with the number of CO moles produced:

$$x = C \int_0^{\tau} \alpha \, d\tau \quad T = \text{const}. \tag{23}$$

The extent of the reaction defined by Téophile de Donder can be used to compare the amount of reacted moles of C and CO_2 with the corresponding number of CO moles produced. In the case of the reaction (1), when λ = const, the following equality can be obtained:

$$\lambda = \frac{n_i - n}{1} = \frac{n_{i,CO_2} - n_{CO_2}}{1} = \frac{n_{CO}}{2} \tag{24}$$

which, for this assumption, is reduced to the equation:

$$x = C \cdot \alpha \cdot \tau \quad T = \text{var}. \tag{25}$$

Therefore, for all experimental temperatures and other fixed experimental conditions, a linear dependence of the conversion degree of the solid phase (x) on the independent variable ($\alpha \cdot \tau$) with slope C should occur (Fig. 5). The relationship is confirmed by the experimental data presented in Fig. 5. It can be seen that with temperature increasing, the coefficient C calculated according to (25) decreases and tends to the value determined on the basis of process parameters according to (22). The low conversion degrees of solid and gaseous phases observed in the low temperatures are the most probably affected by a considerable error. With increasing temperature, increase in deviation from the straight line which resulted from the first measuring point is noticed. It results from the initial mass loss of sample while achieving the assumed temperature of the experiment (pyrolysis), and it is not directly related to the gasification reaction. Hence, uncontrolled mass loss for the first measuring point results from the adopted methodology of the studies and increases with increasing temperature of the process and the volatile matter content in the sample.

From the above equations, Eqs. (21) and (22) were accepted for further utilization, considering the balance (25) as an auxiliary and special case of the reaction/process while maintaining stoichiometry.

Kinetic models for solid-phase conversion with the mass balance

Many kinetic models can be found in the extensive literature devoted to the kinetics of reactions/processes (1) [13–17]. The general form of a kinetic model for the solid phase has the form:

$$\frac{dx}{d\tau} = k \cdot f(x) \tag{26}$$

where on the basis of works [10, 11], the function $f(x)$ frequently corresponds to nth-order kinetics. In the general form, where

$$n = 0, {}^1/_2, {}^2/_3 \text{ or } 1:$$

$$\frac{dx}{d\tau} = k \cdot (1-x)^n \tag{27}$$

or, by taking into account the available reactive surface of the solid phase (random pore model):

$$\frac{dx}{d\tau} = k(1-x)\sqrt{1 - \Psi \ln(1-x)}. \tag{28}$$

According to [11], Eq. (28) includes a kinetic constant that is not presented in the original work [18] because the equation was derived on the basis of dimensionless time.

Structural factor Ψ ($1 \le \Psi \le 8$) can be either determined by detailed studies of pore size distribution and porosity or estimated according to [17] with the possibility of modifying [19].

Comparing Eq. (21) with (27) or (28) leads to the absurd result:

$$C \cdot \alpha = k \cdot (1-x)^n \tag{29}$$

or

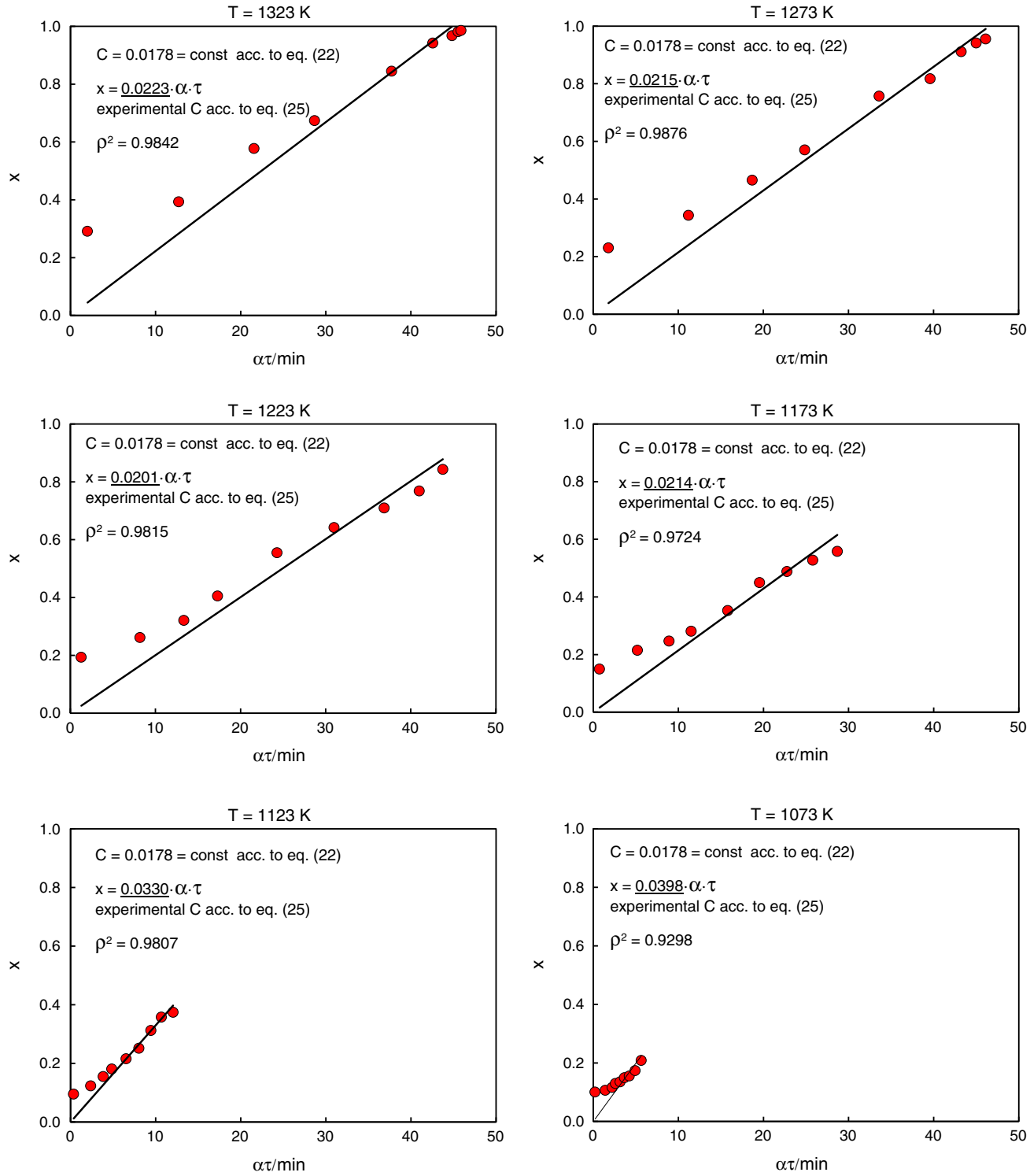

Fig. 5 Dependence of the conversion degree of the solid phase (x) versus the independent variable ($\alpha \cdot \tau$) with the slope C (sample: SLF "Ecocoal")

$$C \cdot \alpha = k(1-x)\sqrt{1 - \Psi \ln(1-x)} \tag{30}$$

because when $\alpha = 0$, $x = 0$. Therefore, in both cases one can obtain $k = 0$. This implies that the initial conditions are divergent in the initial stage of the reaction/process (1). Equations (29) and (30) behave similarly in final state.

Kinetic models for the gaseous-phase conversion with mass balance

Kinetic models for the gaseous phase are more complex and require many assumptions. In general, we are interested in the dependence of CO formation in reaction/process (1). The approach of many authors in this area is too complex for a short discussion. Mianowski et al. [7, 10] introduced a concept based on the established mechanisms (2) and (3), taking into account the separation of a reversible chemical reaction from the desorption process in accordance with the following equation:

$$[\mathrm{CO}] = \frac{k_1}{k_1 + k_{-1} - k_3}[\exp(-k_3\tau) - \exp(-(k_1 + k_{-1})\tau)] \quad k_1 + k_{-1} > k_3. \tag{31}$$

The following relation is obtained from the mass balance in Eq. (23), taking into account the definition in Eq. (6) after the transformation of the integrand function:

$$x = C\left\{-\tau + 2\int_0^{\tau} \frac{d\tau}{2 - [\mathrm{CO}]}\right\}. \tag{32}$$

After inserting Eq. (31) in place of [CO], integral functions are formed. They are difficult to calculate analytically because they are dependent on the kinetic constants, so the integrand has irrational expressions (best substitution: $\tau = -\ln z$, $\mathrm{d}\tau = -\mathrm{d}z/z$).

For these reasons, the balance in Eq. (23) assumes the approximating kinetic function for conversion degree of CO_2 in the typical form for consecutive reactions:

$$\alpha = B(e^{-\mathrm{m}\tau} - e^{-\mathrm{p}\tau}) \quad \text{where} \quad p > m \tag{33}$$

and after integration over the limits $\langle 0; x\rangle$ and $\langle 0; \tau\rangle$, one can obtain:

$$x = C \cdot B\left(\frac{1 - e^{-\mathrm{m}\tau}}{m} - \frac{1 - e^{-\mathrm{p}\tau}}{p}\right) \tag{34}$$

which can be rewritten as:

$$x = C \cdot B\left(\frac{p - m + me^{-\mathrm{p}\tau} - pe^{-\mathrm{m}\tau}}{m \cdot p}\right) \quad \text{where} \quad p > m. \tag{35}$$

Parameters B, m and p in above equations are combination of reaction rate constants.

When we consider that measurements of the initial progress of the reaction/process associated mainly with reaction (2) are not reliable due to the available measurement technique, the initial range can be disabled by assuming the limits of integration $\langle x_i; x\rangle$ and $\langle \tau_i; \tau\rangle$. We finally obtain:

$$x = x_i + C \cdot B\left(\frac{e^{-\mathrm{p}\tau} - e^{-\mathrm{p}\tau_i}}{p} - \frac{e^{-\mathrm{m}\tau} - e^{-\mathrm{m}\tau_i}}{m}\right) \tag{36}$$

Results and discussion

The studies on the gasification with CO_2 were carried out in the Geneva method equipment using the "start–stop" method. Measurements were taken in temperature range 800–1050 °C, for CO_2 flow 150 $\mathrm{cm^3\ min^{-1}}$, and initial mass of all samples was 5 g. Three samples with varying degrees of degassing were used in this study: a typical domestic coke (DC), semi-coke from Lurgi furnace (SC) and smokeless fuel (SLF).

In the case of samples DC and SC, kinetics of slid-phase conversion can be described by zeroth-order model, which after resolving Eq. (27) takes form:

$$x = x_i + k \cdot \tau \quad \text{or when} \quad x_i = 0 \quad x = k \cdot \tau. \tag{37}$$

For SLF zeroth-order model is appropriate in temperature range 800–900 °C, whereas for temperature range 950–1050 °C first-order model ($n = 1$) in form:

$$x = 1 - (1 - x_i)e^{-\mathrm{k}\tau} \quad \text{or when} \quad x_i = 0 \quad x = 1 - e^{-\mathrm{k}\tau}. \tag{38}$$

Figures 6–8 shows the set of experimental data of the conversion degree of the solid phase and the conversion degree of CO_2 as a function of time. The approximated data for α were designated by Eq. (33) and by Eqs. (35) and (36) for solid-phase conversion. In the second case, the experimental value for the maximum conversion of CO_2 was assumed as x_i.

For further consideration, if the nonlinear regression determination coefficient $R^2 < 0.85$, as determined by the Levenberg–Marquardt algorithm, the estimators of equation Eq. (33) were discarded. For such a qualification, data from Figs. 6–8 include:

DC sample (all temperatures) (Fig. 6),
SC sample (950 and 1000 °C) (Fig. 7),
SLF sample (900, 950, 1000 and 1050 °C) (Fig. 8).

The first observation concerns temperature. The estimators of Eq. (33) are more useful for comparison with the kinetics of solid-phase conversion at higher experimental temperatures. The combined Eq. (36) was used for all samples instead of Eq. (35). Applying the concept of a combined relation means that experimentally determined x_i excludes the first dynamic stage of reaction (2) because the analysis of the gaseous phase in this stage suggests a much lower conversion degree of the solid phase.

In the case of DC sample, high correlation of experimental data and designated approximations is observed.

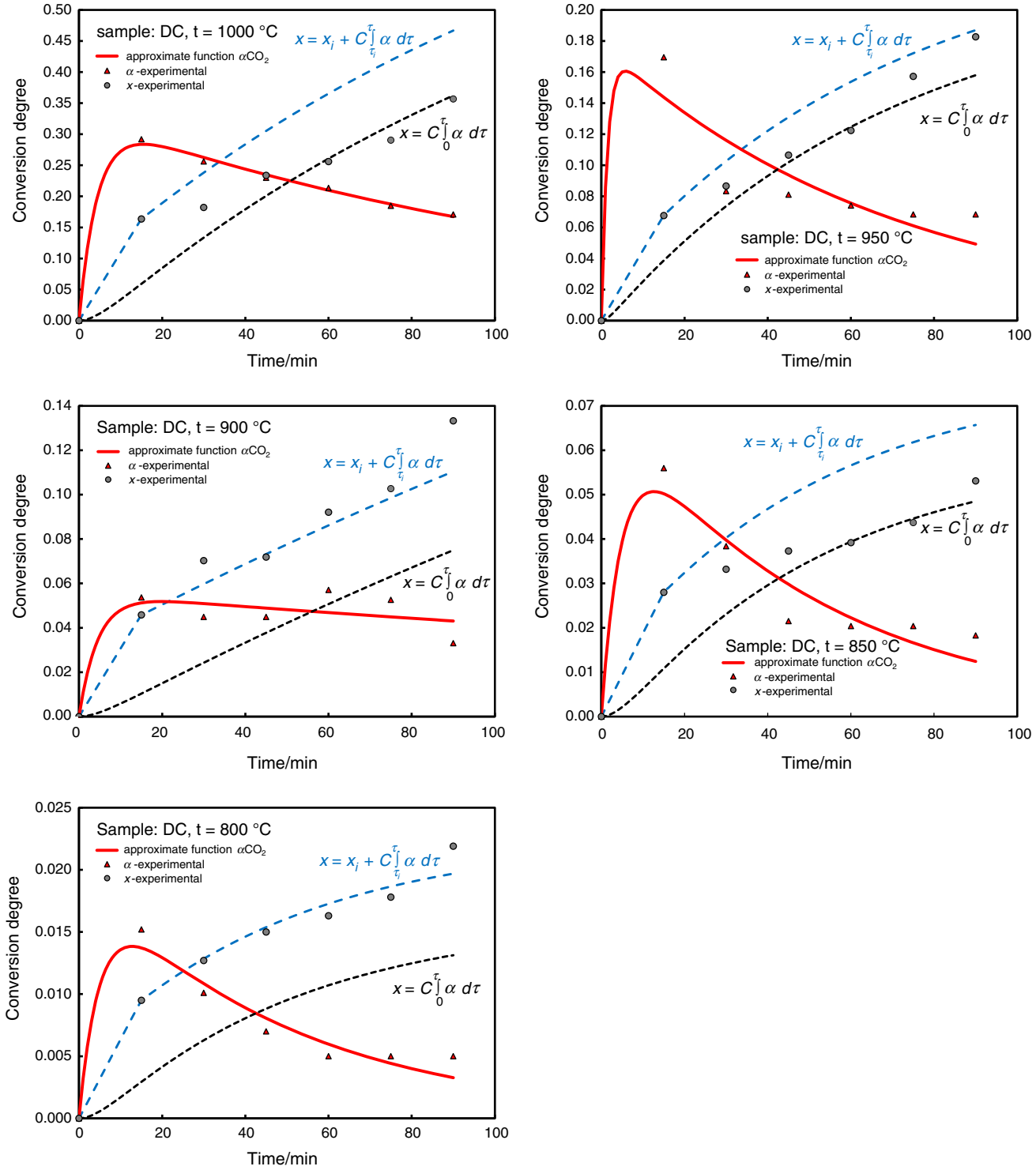

Fig. 6 Dependence of the conversion degree of solid phase (x) and conversion degree of conversion of CO_2 (α) versus time for sample DC

Unfortunately, for SC sample this kind of relation does not occur. It can be easy explain by high volatile matter content and relatively low reactivity of solid phase. Consequently, products of pyrolysis disturbing composition of gaseous phase suggest the higher conversion degree in comparison with actually registered. It should be noted that Eq. (23) assumes the presence of only two gases: CO and CO_2 according to Eq. (5).

Results for SLF sample are interesting in this context. It can easily be observed that at higher temperatures, the

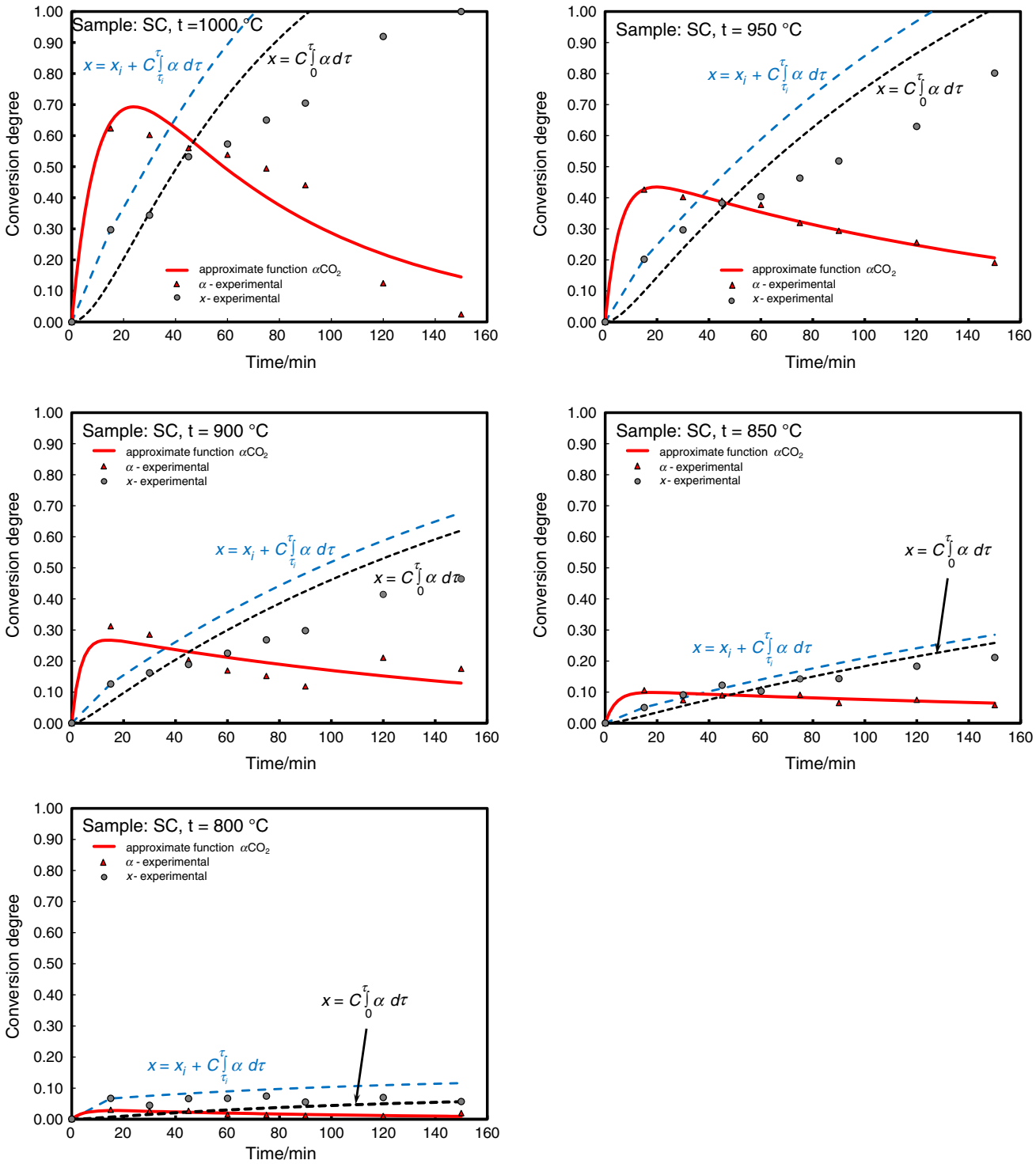

Fig. 7 Dependence of the conversion degree of solid phase (x) and conversion degree of conversion of CO_2 (α) versus time for sample SC

simulation reflects the nature of the change in the solid phase corresponding to first-order kinetics, characteristic of compositions of gaseous coals with a predetermined amount of coking coal, which in plastic stage is a binder in this material.

The second observation is that the results of these studies refer to the interpretation for the second time in this work with reference to (21) with (27) or (28) in which the impact of the initial stage of the reaction/process (1) for gasification kinetics is called into question. Unfortunately,

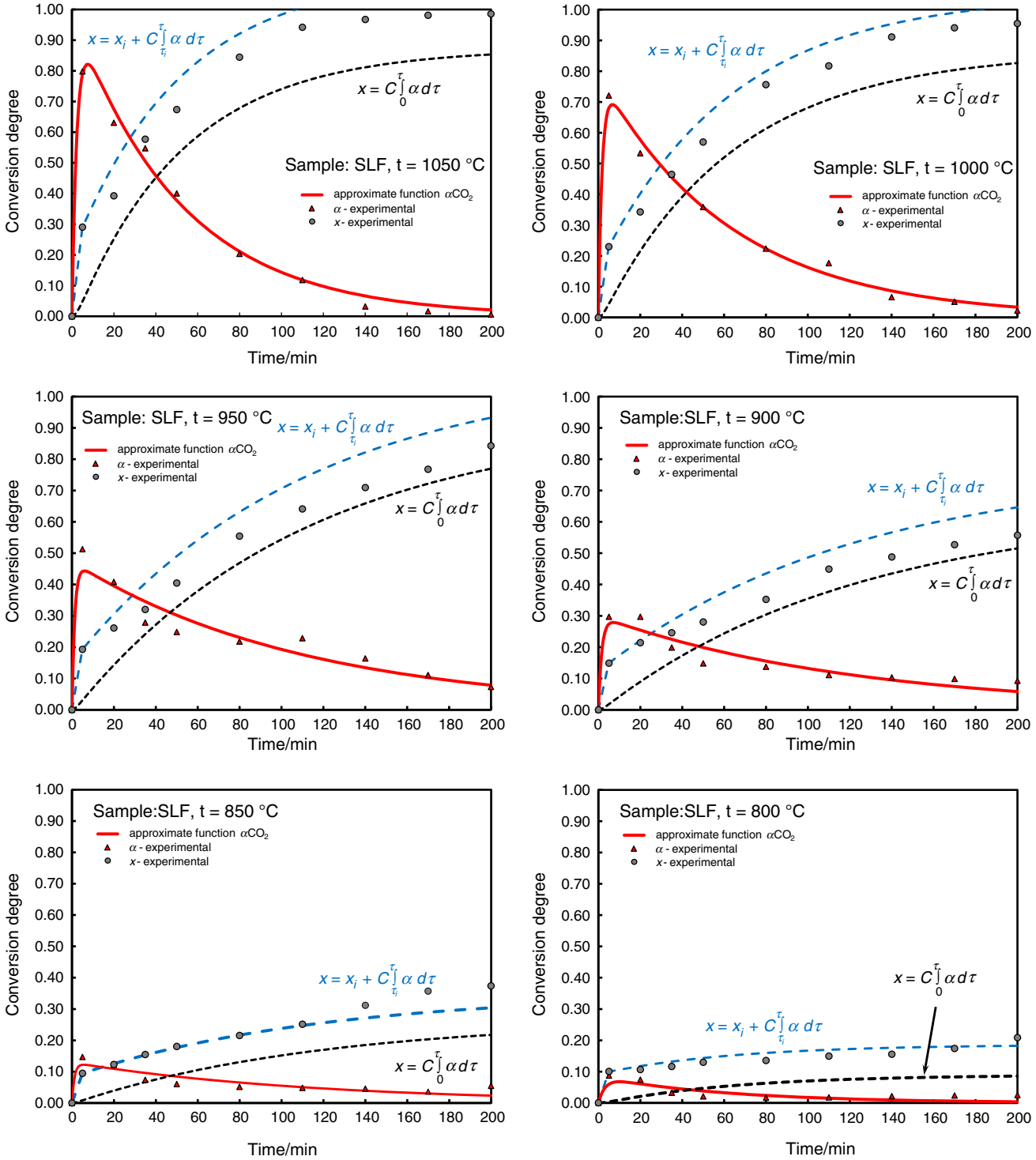

Fig. 8 Dependence of the conversion degree of solid phase (x) and conversion degree of conversion of CO_2 (α) versus time for sample SLF

the results of this study indicate that quantifying the portion of the transition state C(O) according to Eqs. (2) and (3) on the basis of the used measurement technique is not possible. There is a lack of real-time measurement of gas composition and mass in solid phase at the reaction temperature. Determining mass loss by the "start–stop" method can lead to substantive errors resulting from temperature reduction.

Conclusions

1. The apparatus used for determining the reactivity of cokes according to [3] for three selected fuels: domestic coke DC, semi-coke SC and smokeless fuel SLF, in which the composition of the gaseous phase (at the reaction temperature) and mass loss (at ambient temperature), was analyzed using the "start–stop method." It was found that the rate of the reaction/process was related to the rate of increase in the conversion degree of the solid phase, changing in direct proportion to the conversion degree of CO_2 in the gaseous phase according to (20) or (21). The result of this work is consistent with the results obtained in fluidized bed technology (Hambach lignite char, dust 600–1000 μm, Fig. 3 in [20]), but in this study, the conversion of the solid phase was determined experimentally not computationally.
2. The mass balance in the differential Eqs. (20) and (21) has the structure of a kinetic equation, wherein the kinetic constant is replaced by the known process constant ($k = C$). This means that compared to Eq. (27), relationship $C\alpha = k(1 - x)^n$ is obtained, which is divergent from the initial condition when $\tau = 0$, because then $\alpha = 0$ at the same time $x = 0$. A similar result is also observed for the RPM model in Eq. (28). It can be stated here that none of the analyzed kinetic function $f(x)$ fulfills balance in Eq. (20) or (21) for the initial condition. In this regard, the relationship between the conversion degree of CO_2 and time determines the reaction rate related to the conversion degree of the solid phase as a function of time. This dependence usually has a maximum, or less frequently, a horizontal asymptote accompanied by a monotonic increase in the conversion of solid phase.
3. Integral Eq. (21) eliminates the observed inconsistency. However, compared to previous considerations [7] based on the Ergun mechanism [9] described by Eqs. (2) and (3), simplify the equation, the integrand was approximated by the two-element Eq. (33). In this case, the kinetic constant m corresponds to the desorption process of C(O) and the constant ρ is relatively fast for the B–B gasification reaction with the ability to slow down the reaction due to its reversibility and/or inhibition effect. It should be noted that the estimators of Eq. (33) are more reliable with increasing temperature, with $R^2 \geq 0.85$.
4. However, the necessity to use combined relation (36) instead of (35) is often observed. Applying the concept of a combined relation means that experimentally determined x_i excludes the first dynamic stage of reaction (2) because the analysis of the gaseous phase in this stage suggests a much lower conversion degree of the solid phase. It also implies that the initial stage of the reversible chemical reaction (2) has a strong influence on the complete course of the process with desorption (3).
5. This also confirms that the analysis of the gaseous-phase composition is the result of the reaction/process according to the proposed mechanisms (2) and (3), which involve the transition state C(O), while the final result of observation is determined by the kinetics of the conversion degree of the solid phase.
6. The equipment historically used to determine coke reactivity uses the Geneva method and the Dahme–Junker kinetic model [4], which is based on the assumption that the CO_2 conversion rate is linearly dependent on an equivalent time variable, not a real one. This concept is correct only for very well-degassed solid fuels, i.e., cokes with low volatile matter content, for which the kinetic function $g(\alpha)$ is similar for $\alpha \approx 0$. In other cases (e.g., chars, composite fuels), relationships are strongly dependent on real time.

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